

# Features of the Dynamics of the Photoluminescence Spectrum of the $\text{Cu}_3\text{In}_5\text{S}_9$ Crystal with a Change in the Intensity of Laser Excitation

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**Abstract**—Photoluminescence spectra have been studied on the naturally formed surface of a layered  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal when excited by nanosecond laser radiation. At relatively low levels of optical excitation intensity, luminescence quenching was detected near the photon energy of 1.636 eV, in a narrow energy band—118 MeV. This phenomenon is explained by the formation of bound excitons of a triplet nature and their dissociation with the emission of phonons. It is shown that with an increase in the intensity of optical excitation of the crystal, the impurity band of radiation in the crystal disappears. The spectrum of the  $\text{Cu}_3\text{In}_5\text{S}_9$  photocurrent at 295 K is formed by peaks at energies of 1.53 and 1.81 eV. The lifetime of nonequilibrium electrons through fast centers is  $\sim 20$  ns. From the temperature dependence of the electrical conductivity of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal in the range of 110–350 K, the activation energies of two donor levels were determined: 0.28 and 0.76 eV.

**Keywords:**  $\text{Cu}_3\text{In}_5\text{S}_9$ , photoluminescence, photocurrent, electrical conductivity

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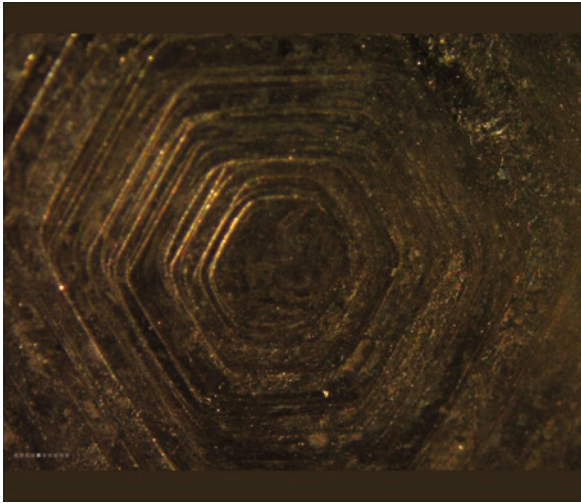
## INTRODUCTION

In the quasi-binary  $\text{Cu}_2\text{S}$ – $\text{In}_2\text{S}_3$  system, a number of ternary compounds ( $\text{CuInS}_2$ ,  $\text{CuIn}_5\text{S}_{11}$ ,  $\text{CuIn}_5\text{S}_8$ ,  $\text{Cu}_3\text{In}_5\text{S}_9$ ) are formed, which are of great practical interest in the field of photonics and as a material for devices designed for photoelectrochemical splitting of water molecules [1–6]. Among these compounds,  $\text{Cu}_3\text{In}_5\text{S}_9$  stands out in some thermodynamic parameters, because it congruently melts at 1083°C and before melting, the compound has one phase state. The crystal structure of  $\text{Cu}_3\text{In}_5\text{S}_9$  has a layered structure that is very different from the structure of the other compounds mentioned above. The spatial group of the crystal structure of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal belongs to the group  $D_{6h}^1$ –( $P6/mmm$ ).

The study of the properties and technology of obtaining 2D crystals stimulated the increased interest of researchers in crystals with a layered structure. The weak connection of the Van-der-Waals character between the layers and the low concentration of surface states on the free surface of the layers make it possible to obtain nanolayers of layered crystals in simple ways and keep them in a stable state during research. These crystals can be mechanically split into nanolayers with a mirror surface. The crystal structure of

$\text{Cu}_3\text{In}_5\text{S}_9$ , as an analogue of the  $\text{Cu}_3\text{In}_5\text{Te}_9$  structure [7], has an 11.4% anionic vacancy of the crystal lattice and certainly belongs to the group of defective crystals. Monocrystalline ingots of the  $\text{Cu}_3\text{In}_5\text{S}_9$  compound are easily mechanically cleaved into plates having a mirror surface perpendicular to the direction of the crystal axis. The layering of the  $\text{Cu}_3\text{In}_5\text{S}_9$  structure makes it possible to obtain plates with a mirror-smooth surface with a low concentration of surface states ( $\sim 10^9 \text{ cm}^{-2}$ ). Such a surface is very popular for obtaining multilayer heterostructures and nanoparticles by chemical deposition on a substrate.  $\text{Cu}_3\text{In}_5\text{S}_9$  crystals have high photosensitivity and highly luminescent properties, like crystals of the defective  $\text{CuIn}_5\text{S}_8$  compound [8].

The photoluminescence spectra of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at temperatures of 4.2–80 K were studied in [6]. The spectra cover the energy range of electromagnetic waves of 1.2–1.6 eV and consist of one gentle peak. The maximum peak of the spectrum at 4.2 is at 1.62 eV and this value is taken as the energy of the band gap of the crystal at a given temperature. The photoluminescence of a  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at room temperature under the influence of a pulse of Nd:YAG laser radiation ( $\lambda = 532 \text{ nm}$ ) on a naturally formed crystal surface is studied.



**Fig. 1.** Microscopic image of the natural surface of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal (magnification X200).

## 1. EXPERIMENTAL TECHNIQUE

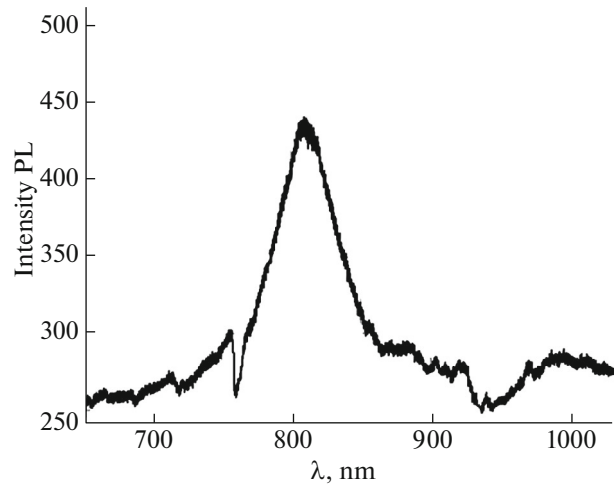
$\text{Cu}_3\text{In}_5\text{S}_9$  crystals were grown by slow cooling of the melt in the horizontal position of the ampoule at a constant temperature gradient. The grown crystals had  $n$ -type electrical conductivity, and hexagonal shapes were formed on their free surface, shown in Fig. 1.

Photoluminescence spectra were taken under the action of pulsed laser radiation. A pulsed Nd:YAG laser (LQ529B) with built-in 2nd and 3rd harmonic generators was used as a radiation source, designed to generate radiation with a wavelength of 1064, 532, 355 nm and with a tunable wavelength in the range from 410 to 710 nm. Pulse duration  $\Delta t = 12$  nanoseconds, pulse energy  $\sim 135$  mJ. The recording of photocurrent and laser radiation pulses was performed using a technique that allows recording single nanosecond pulses on the screen of a storage oscilloscope (LeCroy—wave Jet 354A).

The photoconductivity spectra of the samples with dimensions of  $0.6 \times 2 \times 6 \text{ mm}^3$  were taken in the modes of constant or intensity-modulated illumination at a frequency of 4.8 kHz. The electrical conductivity of rectangular samples provided with lateral ohmic contacts was measured in the crystal cooling mode from 100 to 400 K, in the dark.

## 2. EXPERIMENTAL RESULTS AND DISCUSSION

The photoluminescence spectrum of a  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at 300K excited by the second harmonic ( $\lambda = 532$  nm) of Nd:YAG laser radiation with an intensity of  $4 \times 10^{16}$  quantum/cm<sup>2</sup> s is shown in Fig. 2. As can be seen, numerous structures are manifested on the spectrum. The impurity band of radiation is manifested about 993 nm in the form of a gentle peak. The

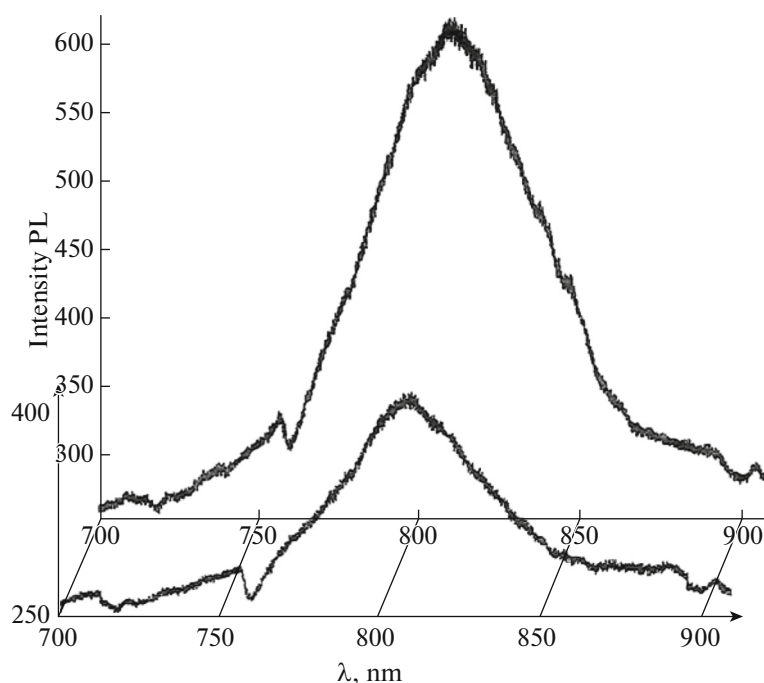


**Fig. 2.** Photoluminescence spectrum of  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at 300 K excited by Nd:YAG laser radiation with an intensity of  $4 \times 10^{16}$  quantum/cm<sup>2</sup> s.

maximum of the spectrum of the main radiation band is at 1.53 eV, which is taken as the values of the band gap of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at room temperature. Particular attention is drawn to the structure at 758 nm (1.636 eV), which expresses the quenching of luminescence in a narrow energy band ( $\sim 118$  meV). In our opinion, under the action of laser radiation, bound excitons of a triplet nature with energy of 1.636 eV are formed in  $\text{Cu}_3\text{In}_5\text{S}_9$ . Dissociation of such excitons occurs non-radiatively, and the released electrons, emitting phonons into the ground state in the conduction band, are captured by donor levels, which subsequently recombine as non-equilibrium charge carriers. The substantiation of this opinion is the work [9], which shows the spectrum of high-frequency dielectric permittivity ( $\epsilon_2$ ), at which  $\epsilon_2$  has a high value at 1.636 eV.

With an increase in the intensity of exciting laser radiation, many structures on the  $\text{Cu}_3\text{In}_5\text{S}_9$  photoluminescence spectrum disappear (Fig. 3). The radiation band expressed by a gentle peak of about 993 nm and peaks in the range of 850–930 nm completely disappear. At the intensities of exciting laser radiation of  $2 \times 10^{18}$  quantum/cm<sup>2</sup> s (front spectrum) and  $6 \times 10^{20}$  quantum/cm<sup>2</sup> s (back spectrum), the change in the intensity of the crystal radiation occurs proportionally over the entire energy range, and the maximum of the spectrum of the main radiation band does not shift. At higher levels of optical excitation of the crystal ( $>10^{22}$  quantum/cm<sup>2</sup> s), the photoluminescence spectra of  $\text{Cu}_3\text{In}_5\text{S}_9$  acquire the form presented in [10].

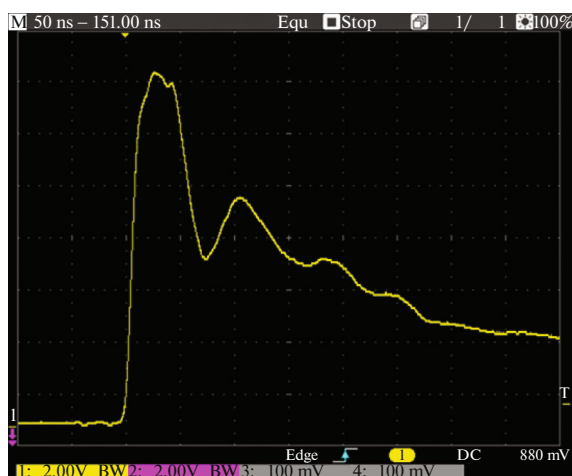
The photoconductivity of  $\text{Cu}_3\text{In}_5\text{S}_9$  crystals was studied in a stationary mode under constant illumination of the crystal and under irradiation with second



**Fig. 3.** Photoluminescence spectrum of  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at 300 K excited by Nd:YAG laser radiation with an intensity of  $2 \times 10^{18}$  quantum/ $\text{cm}^2$  s (front spectrum) and  $6 \times 10^{20}$  quantum/ $\text{cm}^2$  s (back spectrum).

harmonic pulses ( $\lambda = 532$  nm) of Nd:YAG laser radiation with a duration of 12 nanoseconds. The kinetics of the photocurrent when the sample is excited by laser pulses is shown in Fig. 4.

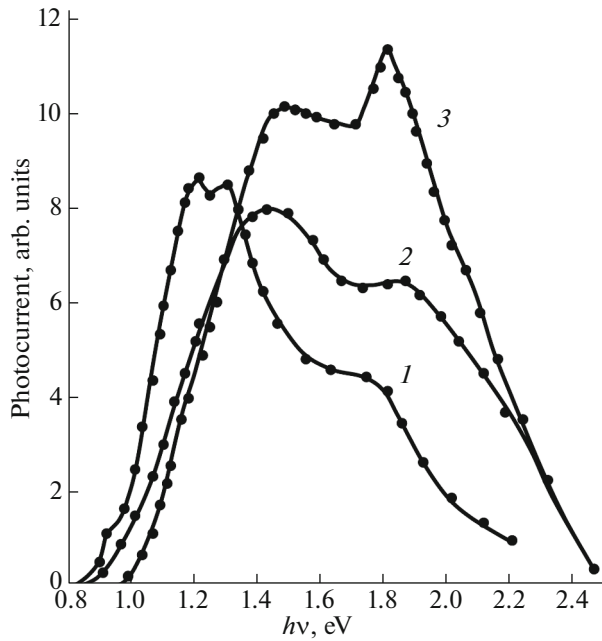
As can be seen, despite the termination of the exciting pulse, an increase in the current level is observed on the photocurrent kinetics curve for some time. This phenomenon can be explained as follows. As noted,



**Fig. 4.** The kinetics of photocurrent in  $\text{Cu}_3\text{In}_5\text{S}_9$  crystals when irradiated with second harmonic pulses ( $\lambda = 532$  nm) of Nd:YAG laser radiation with a duration of 12 nanoseconds.

$\text{Cu}_3\text{In}_5\text{S}_9$  crystals have an 11.6% anionic lattice vacancy and possess *n*-type conductivity. Anionic vacancies of the volatile component of the compound create donor levels, and cationic vacancies create acceptor levels. Therefore, we assume that the crystals contain donor–acceptor pairs with a high concentration. In such cases, under the influence of laser radiation, ionized acceptor impurities are neutralized and after the radiation exposure is stopped, neutral acceptors receive electrons from the valence band and contribute to an increase in the concentration of holes and, consequently, an increase in the current in the crystal. Thus, the current level increases until the capture of electrons by the acceptor centers stops. Current relaxation occurs through fast and slow recombination centers. The lifetime of non-equilibrium electrons through fast centers is  $\sim 20$  ns. During the relaxation of the photocurrent, a damping harmonic oscillation of the current is also observed, apparently due to the formation of a drift capacitance in the crystal under the action of high-intensity laser radiation. A similar phenomenon has been observed in ultrathin InSe films [11], in which the mobility of electrons and holes differ greatly from each other, which contributes to the occurrence of drift capacitance.

The photocurrent spectra given per unit quantum of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at different temperatures are shown in Fig. 5. As can be seen, the spectrum covers the range of electromagnetic radiation 0.9–2.5 eV. The main part of solar radiation on the Earth's surface is

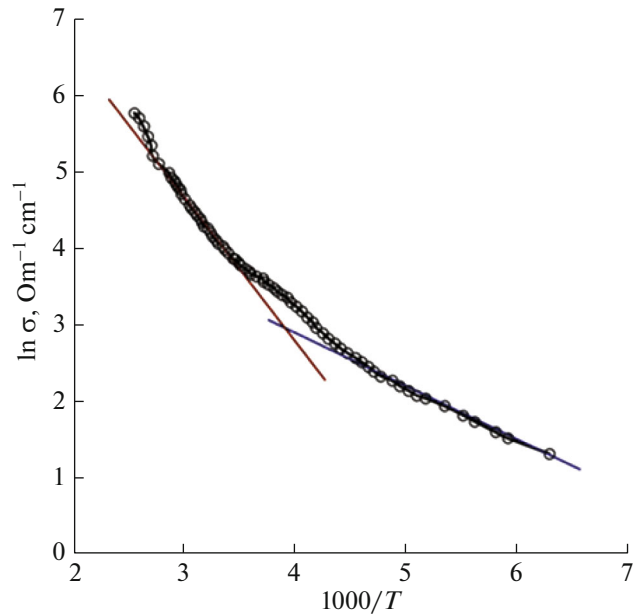


**Fig. 5.** Spectra of the photocurrent of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal at temperatures of 100 (1), 210 (2) and 295 (3) K.

located in this range. Therefore,  $\text{Cu}_3\text{In}_5\text{S}_9$  crystals can be used in the manufacture of highly efficient solar cells. The dynamics of changes in the photocurrent spectrum depending on temperature is complex. At a temperature of 100 K, the edge of the spectrum is sharp (curve 1, Fig. 5) and at 0.96 eV, a structure is observed. The maximum of the spectrum is formed with two peaks at 1.22 and 1.28 eV. Since the band gap of the crystal is 1.55 eV, this means that these peaks are due to impurity photoconductivity.

At temperatures of 210 and 295 K, new peaks appear on the photocurrent spectra and their intensity increases with increasing temperature. The photocurrent spectrum at 295 K is formed by peaks at energies of 1.53 and 1.81 eV. These values are in agreement with the values of energy levels calculated by ellipsometry in the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal [12].

The temperature dependence of the electrical conductivity of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal in the range of 110–350 K is shown in Fig. 6. Activation energies of two donor levels were determined from it: 0.28 and 0.76 eV. At low temperatures, small donor levels are partially in a depleted state. Therefore, at low temperatures, light-excited electrons move from the valence band to local donor levels, creating the photoconductivity of the crystal. Apparently, the photocurrent in the energy range of 0.9–1.5 eV is due to donor and acceptor levels formed by anion-cation vacancies of the crystal lattice.



**Fig. 6.** Temperature dependence of the electrical conductivity of the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal.

## CONCLUSIONS

The photoluminescence spectrum of a  $\text{Cu}_3\text{In}_5\text{S}_9$  layered crystal, taken when exposed to pulsed laser radiation with an intensity of  $4 \times 10^{16}$  quantum/cm<sup>2</sup> s, is formed by radiation bands caused by impurity and intrinsic optical transitions of non-equilibrium electrons. Recombination of non-equilibrium electrons occurs through fast ( $\tau = 20$  ns) and slow channels. With an increase in the crystal temperature from 100 to 295 K, the sensitivity of intrinsic photoconductivity increases. Donor levels with activation energies of 0.28 and 0.76 eV were detected in the  $\text{Cu}_3\text{In}_5\text{S}_9$  crystal, which play an active role in the formation of photoluminescence and photoconductivity spectra.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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